



Comparison between different types of renewable diesel

Stella Bezergianni*, Athanasios Dimitriadis

Centre for Research & Technology Hellas – CERTH, Chemical Process Engineering Research Institute – CPERI, Thessaloniki, Greece

ARTICLE INFO

Article history:

Received 13 July 2011

Received in revised form

25 December 2012

Accepted 26 December 2012

Available online 26 January 2013

Keywords:

Biodiesel

FAME

Green diesel

Fischer–Tropsch diesel

Hybrid diesel

White diesel

ABSTRACT

Renewable fuels, as an alternative fuel, can be produced from different biomass types such as vegetable oils of various origins, waste cooking oils and fats. The most common biofuel is FAME biodiesel that produced via transesterification of vegetable oils. Due to many disadvantages of FAME biodiesel new technologies are under investigation for the production of second generation biodiesel such as Fischer–Tropsch and hydrotreated vegetable oils, waste cooking oils and fats. In the present study the main properties that specify the quality of renewable diesel fuels were examined and a detailed comparison between different types of these fuels was performed. The renewable diesel fuels examined include FAME biodiesel, green diesel, Fischer–Tropsch diesel, hybrid diesel and white diesel.

© 2013 Elsevier Ltd. All rights reserved.

Contents

1. Introduction	110
2. Basic diesel properties	111
3. Description of renewable diesel studied	112
3.1. FAME biodiesel	112
3.2. Green diesel	112
3.3. Fischer–Tropsch biodiesel	113
3.4. White diesel	114
3.5. Hybrid biodiesel	114
4. Renewable diesel comparison	114
5. Conclusions	115
References	115

1. Introduction

Due to the depletion of the world's petroleum reserves and increasing environmental concerns, there is a great demand for alternative sources of petroleum-based fuel, including diesel and gasoline fuels. Biodiesel, a clean renewable fuel, has recently been considered as the best candidate for a diesel fuel substitution because it can be used in any compression ignition engine without the need for modification. Biodiesel is an alternative fuel

similar to conventional or “fossil” diesel [1] which can be produced from raw vegetable oil, animal oils/fats, tallow oil and waste cooking oil. Biodiesel has many environmental beneficial properties as it has the potential to be a “carbon neutral” fuel. Biodiesel fuels are attracting increasing attention worldwide as a blending component or a direct replacement for diesel fuel in vehicle engines [2]. Biodiesel is often used as a blend rather than pure. Biodiesel blends up to B20 can be used in nearly all diesel engines and are compatible with most storage distribution equipment [3,4].

FAME (Fatty Acid Methyl Ester) biodiesel is the most common biofuel employed in Europe and is mainly produced from types of raw vegetable oils from energy crops, but waste oils can also be

* Corresponding author. Tel.: +30 2310 498315; fax: +30 2310 498380.
E-mail address: sbezerg@cperi.certh.gr (S. Bezergianni).

used in small percentages as feedstock. FAME from vegetable oils is considered a first generation biofuel as it is exclusively produced from energy crops using the conventional transesterification technology. The basic feedstock for FAME production is vegetable oil from seeds of various crops such as sunflower, rape, soy, jatropha etc, raising economic and social implications due to the associated “food versus fuel” debate and problematic glycerine disposal. Nevertheless, the growing need for biodiesel and the above considerations directed research focus into alternative technologies that can exploit residual biomass.

As a result, second generation biofuel technologies have been developed to overcome the limitations of first generation biofuels production [5]. The goal of second generation biofuel processes is to extend biofuel production capacity by incorporating residual biomass while increasing sustainability, without undesirable by-products. Residual biomass consists of the crops' residues (such as stems, leaves and husks) and non-food crops (such as switch grass, jatropha, miscanthus and cereals that bear little grain). Furthermore the residual biomass potential can be further augmented by industrial and municipal organic wastes such as skins and pulp from fruit pressing, waste cooking oil [6,7] etc.

As the residual biomass feedstock varies, several second generation biofuels' production processes emerge with significant potential for large-scale applications resulting to different renewable diesel fuels. Fischer–Tropsch diesel is a synthetic diesel produced via the Biomass-To-Liquids route of converting solid biomass into diesel [8]. Green diesel is produced via catalytic hydrotreating of vegetable oils producing a paraffinic diesel fuel, also known as Hydrotreated Vegetable Oil or HVOs [9]. White diesel is produced via catalytic hydrotreating of plain waste cooking oil or WCO [10–12]. Hybrid diesel is produced by co-hydroprocessing of vegetable oils with heavy refinery streams [2,13].

The numerous second generation biofuels' production processes and the versatility of biomass feedstock offer varying characteristics of the corresponding renewable diesel fuels. In this review paper, these fuel properties are presented and compared with those of the conventional FAME biodiesel.

2. Basic diesel properties

This section presents the main fuel properties that affect the quality of diesel fuel [14–17].

Density is a measure of a fuel's mass per unit volume. It is temperature dependent and for diesel fuel is normally determined at 15 °C. As diesel consists of a mixture of many different hydrocarbon compounds of various densities and molecular weights, the overall density depends on the composition of the fuel. Density is strongly correlated with other fuel parameters, particularly cetane number, aromatics content, viscosity and distillation (boiling range or volatility). In diesel engines, the fuel is injected directly into the combustion chamber using a volume based metering system (in most cases). The energy content of the fuel is approximately proportional to the mass of the fuel injected. Thus, for a constant volume injection system, variations in the fuel density can result in variations in the energy content of the fuel injected. Consequently, engine power, emissions and fuel consumption may be affected by the fuel density. In order to optimize the engine performance and exhaust emissions, the fuel density must be controlled within a fairly narrow range.

Sulphur is naturally present in crude oils and must be removed to an acceptable level during the refining process. Sulphur in diesel fuel contributes to the formation of particulate matter (PM) in the engine's exhaust and affects the performance

of vehicle emissions control equipment. It has therefore an indirect effect on emissions of CO, hydrocarbons and NO_x.

Cetane Number (CN) of a fuel is a measure of its propensity for auto-ignition. In practical terms CN has a strong influence on the time interval between the fuel injection and the combustion in a diesel engine. The higher CN, the shorter this ignition delay period is, therefore CN is preferably high. CN affects the ease of starting, the combustion generated noise and the exhaust emissions of diesel engines. **Cetane Index** (CI) is an estimation of CN calculated from the distillation data and density, which according to ASTM D976 is as follows:

$$CI = 454.74 - (1641.416 \times p) + (774.74 \times p^2) - 0.554 \times T50 + 97.803 \times (\log T50)^2$$

where p is the density in g/L at 15 °C and $T50$ is the mid-boiling point temperature in °C (the temperature at which 50% v/v of the sample has evaporated).

Flash point is the lowest temperature at which the vapour above a liquid will ignite when exposed to a flame (or other ignition source with sufficient energy). It is a measure of both volatility and flammability. Flash point is important primarily from the standpoint of safe handling and storage of fuel. Flash point is a reflection of the volatility of the diesel and is therefore set by distillation parameters. It does not affect engine performance directly.

Under ordinary circumstances, diesel fuel appears clear and remains free of **water** and other **sediments**. Water and sediments shortens the life of fuel filters and negatively affects corrosion and microbial growth. Diesel fuel can have a maximum 200 ppm of water and 10 ppm of sediments and still be of good quality.

Carbon residue is a measure of the tendency of diesel to form carbonaceous deposits in engines, which can result in hot spots leading to stress, corrosion or cracking of components. The deposits of most concern are those which build up in the nozzles of fuel injectors. The amount of carbon in fuel can be correlated with a tendency to form deposits, hence the use of a Carbon Residue test. The test is performed on the residual volume after 90% of the fuel has been boiled off (10% residual).

Viscosity is a measure of a fuel's resistance to flow. It affects the performance of diesel fuel pumps and injection systems. Viscosity is dependent on fuel composition and so is reflected in the distillation parameters, density and cold flow properties. The current test method, ASTM D445, measures the kinematic viscosity at 40 °C in centistokes. High viscosity may lead to insufficient fuel flow while very high viscosity may cause fuel pump distortion. Low viscosity will increase leakage from the pumping elements within the pump, which will result in insufficient fuel delivery and hot starting difficulties.

Copper strip corrosion test is a measure of the corrosivity of the fuel to metals. Corrosion can affect metallic components in vehicle fuel systems, dispenser pumps and fuel storage systems and is measured in order to provide protection for fuel tanks, dispenser pumps and vehicle engine components. The test procedure used for the measurement of copper strip corrosion is the ASTM D130 method.

The general **appearance** and **colour** as well as diesel clarity are useful indicators of contamination.

Polyaromatic hydrocarbons (PAH) are compounds containing multiple aromatic rings and no heteroatoms. Whereas single-ring-aromatic (benzenes) are an issue with petrol, it is primarily PAHs that are of concern with diesel. Current evidence suggests that only the PAHs contribute to particulate emissions, so it is only these and not total aromatics in diesel which need to be considered for regulation.

Oxidation Stability or induction time is an indication of the aging rate of a fuel. It is estimated via the Rancimat test which

measures the time required for the formation of gums and sediments (causing plugging of filters and engine deposits) after accelerated oxidation. The oxidation stability shows the threshold for storage and utilization period after the production of a fuel.

Distillation curve (temperature vs. percentage volume recovered) characterizes the volatility of the fuel. T85 is the temperature at which 85% of the fuel sample has boiled off. For diesel, the most important distillation characteristics are the temperatures at the top end of the range (T85, T90, T95 etc.) as these provide a measure of the proportion of heavier components, and correlate closely with levels of aromatics in particular. As the distillation is dependent on the composition of the fuel, it affects density viscosity and cetane index rendering the distillation curve as an important factor in the control of fuel quality. The distillation curve is estimated via ASTM D86.

Heating value is the heat released when a fuel undergoes complete combustion with oxygen under standard conditions for high (gross) heating value, the water produced by the combustion is assumed to be recondensed to liquid. For the lower (net) heating value, water remains in the gas phase. Since engines exhaust water in gas phase, the net heating value is the appropriate value for comparing fuels. The three main factors that affect vehicle fuel economy, torque, and horsepower are the type of engine (i.e. gasoline or diesel), the efficiency of the engine turning energy in the fuel into usable work, and the fuel's volumetric energy content or heating value.

Cold filter plugging point (CFPP) is the lowest temperature at which the fuel can pass through a standard test filter under standard conditions. CFPP is more precise and is a better indication of fuel performance in an engine. The test method is specified in IP 309.

Cloud point is the temperature at which wax crystals start to precipitate out and the fuel becomes cloudy. Cloud point is determined according to the test method specified in ASTM D2500.

Pour point is the lowest temperature at which oil will flow. This property is crucial for fuels that must flow at low temperatures. A commonly used rule of thumb when selecting fuels is to ensure that the pour point is at least 10 °C (20 °F) lower than the lowest anticipated ambient temperature.

3. Description of renewable diesel studied

3.1. FAME biodiesel

Fatty-Acid Methyl Esters or FAME is obtained from vegetable oil or animal fats (bio-lipids) which have been transesterified with an alcohol. The transesterification process is simply described as the chemical breaking of fatty acids contained in vegetable oils using alcohol to form alcohol esters and glycerol [18], targeting to lowering the viscosity and volatility of vegetable oil. Although ethanol is the preferred alcohol for transesterification due to its renewable biomass origin and lower toxicity level [19], methanol is most commonly used due to its price competitiveness compared with other common alcohols such as ethanol and isopropanol. This leads to the predominance of fatty acid methyl esters (FAME) [20].

FAME can be produced from many types of oils, the most common being rapeseed oil (rapeseed methyl ester, RME) in Europe and soybean oil (Soya methyl ester, SME) in the USA. In the transesterification processes catalysts such as sodium or potassium hydroxide are employed to convert vegetable oil and methanol into FAME. Moreover, during transesterification undesirable by-products (glycerine and water) are also formed. By-products must be removed from the final product along with

methanol traces. FAME can be used in diesel engines where the manufacturer approves such use but it is more often used as a mix with conventional diesel [21].

FAME biodiesel quality was standardized via international standard methods such as ASTM and EN. In Europe, biodiesel blended in diesel is mandatory in many countries and thus available at many service stations. The world biodiesel production output was estimated to be 11 million metric tonnes in the year of 2008, which reached 20 million metric tonnes in 2010.

The main factor determining the current cost of biodiesel production is the feedstock cost which can be as high as 88% of the total production cost [22]. However, total production cost can be greatly reduced by lowering the cost of feedstock with the use of more economical alternatives such as waste fats or oils, which however lower the FAME quality characteristics.

According to Table 1 FAME biodiesel has very good fuel properties as a diesel substitute. Thus, the results show that biodiesel can be used in a wide variety of applications. The heating value of FAME biodiesel ranges between 37 and 40 MJ/kg which meets the diesel standards. FAME biodiesel has density ranging between 0.85–0.9 g/ml which also meets the diesel–biodiesel international standards. Moreover, the sulphur content of FAME biodiesel is very low. Furthermore, it has a good cetane number (45–73), which indicates good auto-ignition quality. The flash point of FAME biodiesel varies from 96 to 188 °C while it presents a satisfactory CFPP (min – 13 °C). It has very high water content which shortens the life of fuel filters and affects negatively the corrosion. Viscosity of FAME is also high, that provides insufficient lubrication to diesel engines [23–27].

3.2. Green diesel

Green diesel, also known as renewable diesel, is a diesel substitute of renewable origin (vegetable oils and fats). Green diesel should not to be confused with biodiesel (FAME) as it is produced via catalytic hydroprocessing of vegetable oils and fats [28] and not transesterification.

Catalytic hydroprocessing is a common refinery process aiming to increase hydrogen to carbon ratio, decrease the concentration of heteroatoms and metals, and reduce the boiling point of petroleum fractions. Catalytic hydroprocessing of vegetable oils is focused on producing a high quality biodiesel product that is compatible with existing diesel fuel infrastructure. The Green diesel technology consists of two steps, one catalytic hydrotreatment step which will produce normal paraffins, and one catalytic isomerization step which will lead to a mixture of n- and iso-paraffins [29].

Green diesel consists mainly of paraffins and is free of aromatics, oxygen and sulphur. As a result, this paraffinic fuel has higher cetane number and higher heating value compared to FAME. Another advantage is that catalytic hydroprocessing leaves no by-products, unlike FAME which is accompanied by glycerine. Furthermore, as hydroprocessing includes desulphurization reactions, Green diesel is a low sulphur fuel (< 10 ppmwt) with very low green house gas emissions (GHG) [30]. Green diesel can be produced from several types of vegetable oil without compromising fuel quality, while rapeseed and palm oil are the most commonly used.

The cetane number of green diesel ranges between 80 and 99, which is much higher compared to diesel standards, rendering it a competitive diesel substitute. The density range of green diesel is 0.77–0.83 g/ml which also meets the diesel–biodiesel standard [31–33]. Its net heating value is between 42 and 44 MJ/kg, which is almost similar to that of conventional diesel [34,35], while its low aromatic content (< 0.1%wt) leads to cleaner combustion according to Aatola [35]. Regarding its cold flow properties, its

Table 1
Properties of different types of renewable diesel.

Analysis	Units	White diesel	FT diesel	FAME biodiesel	Green diesel (HDO VO)	Hybrid diesel (VGO+VO)	Fossil diesel	Diesel standard Min/Max	
Density	g/ml	0.79	0.72–0.82	0.855–0.9	0.77–0.83	0.781–0.85	0.85	Min 0.8	Max 0.845
Sulphur	mg/kg (ppmwt)	1.54	< 10	0–0.012	< 10	3–13	12		Max 10
Cetane Index		77.23	70	58.3	50–105	51–64	54.57	Min 46	
Cetane number			55–99	45–72.7	80–99	50–101	50	Min 51	
Flash point	°C	116	55–78	96–188	68–120	74–105	52–136	Min 60	Max 170
Water	mg/kg	13	19	28.5–500	42–95	10–50	0.5		200
MCRT carbon residue	(Wt%) %m/m	0.0066	0.02–4.5	0.02–0.3		85.8			Max 0.3
VISCO 40 °C	cSt	3.5	2.1–3.5	3.89–7.9	2.5–4.15	2.7–5.5	2.71	Min 2	Max 4.5
Cooper strip corrosion	(3 h in 50 °C)	1b		1			< 3	class 1	–
Colour	(ASTM)	0			~2				–
HPLC	%wt (%m/m)		0		< 0.1	0.1–1.2		< 11	–
Induction time (oxidation time) (110 °C)	h	> 22	> 22	0.9–10.9	> 22	> 22		Min 6	–
Distillation 90 vol% °C	°C	302.6	295–335		298–342	300–332	341	85–360	–
Net heating value	MJ/kg	49	43–45	37.1–40.4	42–44	43.3–47	34.97	Min 35	–
CFPP	°C	20	(–22)–0	(–13)–15	> 20	(–24)–22	–6	–5	+5
Cloud point	°C		(–25)–0	(–3)–17	(–25)–30	(–23)–20	–5	Min –5	Max 12
Pour point	°C	23		(–15)–16	(–3)–29	(–26)–20	–21	Min –13	Max 10

pour point ranges from –1 to 29 °C while its cloud point is from –25 to 30 °C. Finally, green diesel has a flash point of 68–120 °C, thus it is safe for handling and storage.

Green diesel is a new biofuel which however is currently produced in industrial scale. The first commercial scale hydro-processing plant with a capacity of 170,000 t per year was started up in summer 2007 at Neste Oil's Porvoo oil refinery in Finland. This technology is branded as "NExBTL" [36].

3.3. Fischer–Tropsch biodiesel

The Fischer–Tropsch (FT) diesel is a synthetic diesel which results from the FT-synthesis technology pioneered by the Germans in the 1920s. This technology was originally aimed at producing hydrocarbon molecules from coal [37]. The Fischer–Tropsch process (or Fischer–Tropsch Synthesis) is a set of chemical reactions of synthesizing hydrocarbons from a mixture of carbon monoxide and hydrogen. The process, a key component of gas to liquid technology, produces a petroleum substitute, typically from coal, natural gas, or biomass for use as synthetic lubrication oil and as synthetic fuel. Recently the F–T process became compatible with biofuels as it was incorporated in an overall biomass to liquid (BTL) scheme, which converts the synthesis gas ($\text{CO} + \text{H}_2$) of residual biomass gasification to synthetic biofuels.

There are two main classes of commercial Fischer–Tropsch technology, namely, Low-Temperature Fischer–Tropsch (LTFT) and High-Temperature Fischer–Tropsch (HTFT). LTFT operation requires lower temperatures and uses a cobalt based catalyst. The wax and hydrocarbon condensate produced by the low temperature Fischer–Tropsch process is predominantly linear paraffins with a small fraction of olefins and oxygenates [38]. The consecutive upgrading via catalytic hydrogenation of olefins and oxygenates and via the catalytic hydrocracking of wax to naphtha and diesel can be done at relatively mild conditions. This process is best known for being used in the first integrated Gas-to-Liquid (GTL) plant operated and built by Shell in Bintulu, Malaysia [39]. HTFT operation employs higher temperatures (330–350 °C) and uses iron-based catalysts [39]. The HTFT process is used primarily for the production of liquid fuels such as the LTFT process. The most critical HTFT distillate characteristics are their cold flow properties, which are inherently high because of the high paraffin content, and low density [40]. The Fischer–Tropsch technology

was adopted by Sasol in South Africa and has since been optimized, resulting in the largest Coal-To-Liquid (CTL) facility of this type in the world [39].

Current developments focus on producing clean Fischer–Tropsch fuels based on biomass. For the production of Fischer–Tropsch liquids from residual biomass, a slurry reactor or a fixed bed reactor is normally used as synthesis reactor. In such applications both iron or cobalt catalysts can be used. Cobalt catalysts have a higher conversion rate, a longer life, and a higher reactivity, while the iron catalyst type has a higher tolerance for impurities and a lower price. Moreover, iron-based catalysts show considerable water-gas shift (WGS) activity and the H_2/CO ratio is adjusted in the synthesis reactor.

Fischer–Tropsch liquids can be produced from several types of biomass. For the production of 1 t of Fischer–Tropsch diesel about 8.5 t of wood are needed [41]. In October 2006, the Finnish paper and pulp manufacturer UPM (Biofore Company) announced its plans to produce biodiesel by the Fischer–Tropsch process alongside its manufacturing processes, using residual biomass produced by the paper and pulp manufacturing processes [42].

This Fischer–Tropsch biodiesel is similar to fossil diesel regarding its energy content, density, viscosity and flash point. It's a high quality and clean transportation fuel with favourable characteristics for application in diesel engines [43]. The Fischer–Tropsch biodiesel fuel properties' range is listed in Table 1.

Fischer–Tropsch biodiesel's density is between 0.72 and 0.82 g/ml which meets the diesel–biodiesel international standards [28,34,40,44–47]. Moreover, it has a very low aromatic content, which leads to cleaner combustion (0–0.1%wt) [35,36,40] as the particle and NO_x exhaust emissions are lower. Furthermore, there are no sulphur emissions, since Fischer–Tropsch biodiesel is a low sulphur fuel (<10 ppmwt). It should be noted that Fischer–Tropsch diesel has a high cetane number (55–99), which indicates better auto-ignition quality. Furthermore it has high oxidation stability as its reported induction time is high ~75.5 h [31], therefore it does not need anti-oxidant additives as it is required by FAME biodiesel which exhibits low oxidation stability due to its low levels of natural anti-oxidants. The heating value of Fischer–Tropsch diesel ranges between 43 and 45 MJ/kg, which is higher compared to diesel and biodiesel standards making it an attractive diesel fuel substitute. Flash point is low, which raises the chances for auto-combustion [39,43–45]. Finally the viscosity is within specifications as it ranges between 2.1 and 3.5 cSt.

3.4. White diesel

White diesel is the product of catalytic hydrotreatment of 100% waste cooking oil (WCO), and consists of a single catalytic hydrotreatment step. White diesel technology was developed and demonstrated in the pilot-plant facilities of the Chemical Process and Energy Recourses Institute (CPERI) of the Research and Technology Hellas (CERTH) [11,12,48]. The white diesel technology was demonstrated via the BIOFUELS-2G environmental project as it was employed for the operation of a regular garbage truck from the fleet of the Municipality of Thessaloniki, Greece [49].

White diesel is a paraffinic fuel, free of sulphur and aromatics. As catalytic hydrotreatment targets in heteroatom removal, white diesel has negligible sulphur levels of ~ 1.54 wppm. Moreover, it has a low density of 79 gr/ml, which is lower compared to diesel and biodiesel standards [3,15]. This means that a higher fuel volume must be supplied for the same amount of energy compared to diesel. However, as a lower density fuel, it has the potential to reduce the level of smoke [50]. The cetane number of white diesel is very high according to Fig. 1, and other properties are very similar to other biofuels referred above.

White diesel has increased oxidation stability of > 22 h [51], compared to diesel and biodiesel standards [16], which means that white diesel does not need anti-oxidant additives to meet the satisfactory level of oxidation stability like diesel fuels with low levels of natural anti-oxidants. Furthermore white diesel is also very safe to use and has significantly high flash point (116°C).

The cold flow properties of white diesel are its major drawback (Table 1), which can be overcome either by a second isomerization step (which will increase its production cost) or by blends with conventional diesel. It should be noted that for the demonstration in the garbage truck, 50–50 blends of white diesel with conventional market diesel were used, without any operational problems.

3.5. Hybrid biodiesel

Besides hydroprocessing of vegetable oil in order to produce diesel-range hydrocarbons, there is an option of vegetable oil co-processing with petroleum-derived raw materials. This solution allows utilization of existing refinery technologies, i.e. catalytic hydroprocessing and equipment by integrating liquid biomass into typical refining operations for the production of hybrid fuels.

Several types of vegetable oil can be employed for co-processing with petroleum streams such as soy-been oil rapeseed

oil but also coconut, palm and Jatropha oil [52] and WCO [13]. The few co-processing studies show that the vegetable oil component increases the overall hybrid diesel yield [52,53].

Hybrid diesel density ranges from 0.78 to 0.85 g/ml while the 90%v/v distillate temperature is within $300\text{--}330^\circ\text{C}$. Moreover, kinetic viscosity varies within diesel specifications (2.7–5.5 cSt), cetane number is significantly high (50–101) as is also the net heating value (43.3–47 MJ/kg). The cold flow properties are also quite diverse based on the catalyst and operating parameters employed, for example pour point is between -20 and 26°C and cloud point ranges between -23 and 20°C [10,35,54,55]. Furthermore, the hybrid diesels are also low sulphur (3–13 ppmwt) and aromatics free (0.1–1.2%wt) fuels, thus they can be considered “clean fuels”. Finally, catalytic co-hydrocracking technology may be more suitable as the cracking, treating and isomerization reactions result in a hybrid diesel fuel of better cold flow temperature properties.

4. Renewable diesel comparison

In this section a complete comparison between different kinds of renewable diesel will be discussed. According to Table 1 as far as the density is concerned, all the different types of biodiesel meet the biodiesel standards which range between 0.7 and 0.86 g/ml. This is promising for all technologies examined as density is a very important parameter for biodiesel quality since it defines the level of smoke and engine power.

Diesel and biodiesel fuels must have low sulphur content as the presence of sulphur causes SO_x emissions. Furthermore, sulphur in diesel fuel contributes to the formation of particulate matter (PM) in engine exhaust and affects the performance of vehicle emissions control equipment. The biodiesel types examined have low sulphur content as the maximum observed value does not exceed 13 wppm, which is the case for hybrid biodiesel. FAME and white diesel have the lowest sulphur contents, which gives them an advantage over the other biodiesel types.

Cetane Index (CI) and Cetane Number (CN) have a strong influence on the time interval between the fuel injection and the combustion in a diesel engine. In other words, high CI and CN values favour engine performance. Green diesel and white diesel have the highest CI values as compared with the other kinds of biodiesel (Fig. 1), which is attributed to their high-paraffinic character. Fossil diesel has CI values that often are below threshold and require cetane improver additives, while white diesel has CI of ~ 77 and Green diesel CI values range from 50 to 105.

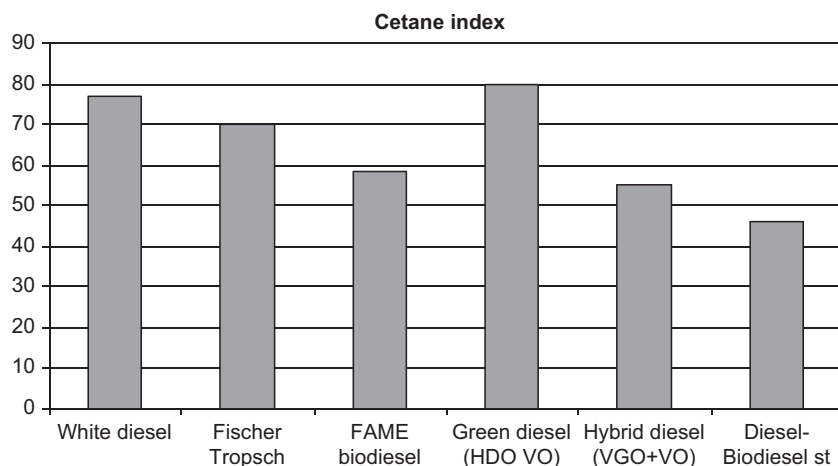


Fig. 1. Cetane index of different types of renewable diesel.

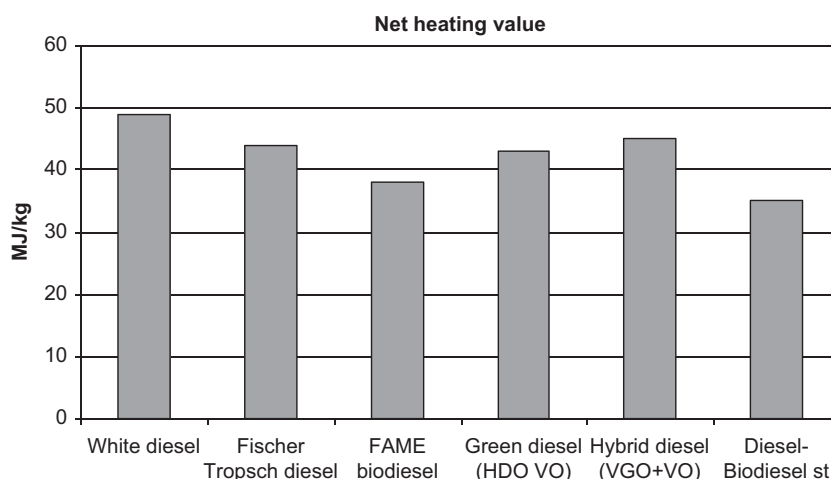


Fig. 2. Net heating value of different types of renewable diesel.

Flash point is another important factor for fuel evaluation, as it characterizes the ability of safe handling and storage. All kinds of biodiesel meet the diesel/biodiesel standards for flash point. As far as the water content is concerned, white diesel has the lowest water content which renders it as the less corrosive biofuels among those compared.

Oxidation stability is one of the most problematic properties of 1st generation biodiesel such as FAME, as it derives from the presence of oxygenates in biodiesel resulting from their biomass origin. However, the oxidation stability of white diesel, green diesel, Fischer–Tropsch diesel and hybrid biodiesel are all exceptionally high, since they involve catalytic hydroprocessing which leads to hydro-deoxygenation.

All types of biodiesel have very low viscosity between 2 and 4 cSt which are in accordance to diesel/biodiesel standards. Moreover white diesel has the lowest carbon residue between the five different kinds of biodiesel.

According to bibliography the net heating value is the appropriate value for comparing fuels, from Fig. 2 it should be noticed that white diesel has the highest net heating value (49 MJ/kg) as hydrotreating process rise the H/C ratio, that means white diesel has shorter ignition delays that provide more time for the fuel combustion process to be completed making it more competitive as a fuel.

The disadvantage of white diesel is the cold properties. Pour point, cloud point and CFPP describe the cold properties of a fuel. White diesel has the highest pour point and CFPP, which is more than 20 °C. This is a problem that can be solved via additives improvers. The distillation (90 vol%) for White diesel is 300 °C in comparison to other type of biodiesel which range from 300 to 340 °C, which means that white diesel consist of lighter molecules than the others. To conclude, white diesel is a very competitive diesel substitute compared to other biodiesel types.

5. Conclusions

Biofuels are becoming a prominent source of transportation energy, especially since their production process ensures sustainability and economic growth. The literature contains hundreds of references of biodiesel production from wide variety of feedstocks and technologies. In this article the properties of different kind of biodiesel are summarized. Biodiesel referred to this article are Fischer–Tropsch diesel, FAME diesel green diesel, hybrid diesel, white diesel and diesel and biodiesel standards. White diesel,

green diesel, hybrid diesel and Fischer–Tropsch have superior properties versus 1st generation FAME biodiesel. Moreover, hydroprocessing technology seems to be more beneficial than transesterification technology of 1st generation FAME biodiesel as it produce no byproduct and can be used in the existing infrastructure of the refineries without the needs of new investments. Finally, from the comparison of all different biodiesel technologies that have been studied in this article, white diesel technology appears to be more willing one as it depends only on renewable residual biomass.

References

- [1] Dennis Leung YC, Xuan Wu, Leung MKH. A review on biodiesel production using catalyzed transesterification. *Applied Energy* 2010;87:1083–95.
- [2] Dermibas A. Progress and recent trends in biodiesel fuels. *Energy Conversion and Management* 2009;50:14–34.
- [3] Mustafa B. Potential alternatives to edible oils for biodiesel production—a review of current work. *Energy Conversion and Management* 2011;52:1479–92.
- [4] Mofijur M, Masjuki HH, Kalam MA, Hazrat MA, Liaquat AM, Shahabuddin M, et al. Prospects of biodiesel from jatropha in Malaysia. *Renewable and Sustainable Energy Reviews* 2012;16:5007–20.
- [5] Naik SN, Goud V, Rout K, Dalai K. Production of first and second generation biofuels: a comprehensive review. *Renewable and sustainable Energy Reviews* 2010;14:578–97.
- [6] Basheer Diya' uddeen H, Abdul Aziz AR, Daud WMAW, Chakrabarti MH. Performance evaluation of biodiesel from used domestic waste oils: a review. *Process Safety and Environmental Protection* 2012;90:164–79.
- [7] Bezergianni S, Kalogianni A, Dimitriadis A. Catalyst evaluation for waste cooking oil hydroprocessing. *Fuel* 2012;93:638–41.
- [8] Swain PK, Das LM, Naik SN. Biomass to liquid: a prospective challenge to research and development in 21st century. *Renewable and Sustainable Energy Reviews* 2011;15(9):4917–33.
- [9] Kubičková I, Kubička D. Utilization of triglycerides and related feedstocks for production of clean hydrocarbon fuels and petrochemicals: a review. *Waste and Biomass Valorization* 2010;1:293–308.
- [10] Bezergianni S, Dimitriadis A, Kalogianni A, Pilavachi PA. Hydrotreating of waste cooking oil for biodiesel production. Part I: Effect of temperature on product yields and heteroatom removal. *Bioresource Technology* 2010;101:6651–6.
- [11] Bezergianni S, Dimitriadis A, Sfetsas T, Kalogianni A. Hydrotreating of waste cooking oil for biodiesel production. Part II: Effect of temperature on hydrocarbon composition. *Bioresource Technology* 2010;101:7658–60.
- [12] Bezergianni S, Dimitriadis A, Kalogianni A, Knudsen KG. Toward hydrotreating of waste cooking oil for biodiesel production. Effect of pressure, LHSV and H_2 /oil ratio, and liquid hourly space velocity. *Industrial Engineering Chemistry Research* 2011;50:3874–9.
- [13] Bezergianni S, Dimitriadis A. Temperature effect on co-hydroprocessing of heavy gas oil-waste cooking oil mixtures for hybrid diesel production. *Fuel* 2013;103:579–84.
- [14] Ministry of Economic Development (Internet source: <<http://www.med.govt.nz>>).

- [15] Shaine Tyson K. Biodiesel handling and use guidelines. National Renewable Energy Laboratory; September 2001.
- [16] Backunder on renewable fuels for diesel engines; June 29 2006.
- [17] Knothe Gerhard. Biodiesel and renewable diesel: a comparison. *Progress in Energy and Combustion Science* 2010;36:364–73.
- [18] Tashtoush G, Al-Widyan MI, Al-Shyoukh AO. Combustion performance and emissions of ethyl ester of a waste vegetable oil in a water-cooled furnace. *Applied Thermal Engineering* 2003;23:285–93.
- [19] Demirbas A. Relationships derived from physical properties of vegetable oil and biodiesel fuels. *Fuel* 2008;87:1743–8.
- [20] Oh Pin Pin, Nang Lau Harrison Lik, Junghui Chen Mei Fong, Chong Yuen May Choo. A review on conventional technologies and emerging process intensification (PI) methods for biodiesel production. *Renewable and Sustainable Energy Reviews* 2012;16:5131–45.
- [21] Robert Bosch GmbH Staff. Bosch automotive handbook, 6th ed. John Wiley & Sons Inc.; 2004. p. 327–8.
- [22] Arvidsson R, Persson S, Froling MN, Svanstrom M. Life cycle assessment of hydrotreated vegetable oil from rape, oil palm and Jatropha. *Journal of Cleaner Production* 2011;19:129–37.
- [23] Jo-Han Ng, Hoon Kiat Ng, Gan Suyin. Advances in biodiesel fuel for application in compression ignition engines. *Clean Technologies Environmental Policy* 2010;12:459–93.
- [24] Rottig A, Wenning L, Broker D, Steinbuchel A. Fatty acid alkyl esters: perspective for production of alternative biofuels. *Applied Microbiology Biotechnology* 2010;85:1713–33.
- [25] Karmakar A, Karmakar S, Mukherjee S. Properties of various plants and animals feedstocks for biodiesel production. *Bioresource Technology* 2010;101:7201–10.
- [26] Rashid U, Anwar F, Knothe G. Evaluation of biodiesel obtained from cottonseed oil. *Fuel Processing Technology* 2009;90:1157–63.
- [27] Amin S. Review on biofuel oil and gas production processes from microalgae. *Energy Conversion and Management* 2009;50:1834–40.
- [28] Lapuerta M, Armas O, José Hernandez J, Tsolakis A. Potential for reducing emissions in a diesel engine by fuelling with conventional biodiesel and Fischer–Tropsch diesel. *Fuel* 2010;89:3106–13.
- [29] Krar M, Kovacs S, Kallo D, Hancsok J. Fuel purpose hydrotreating of sunflower oil on CoMo/Al₂O₃ catalyst. *Bioresource Technology* 2010;101:9287–93.
- [30] Simacek P, Kubicka D, Sebor G, Pospisil M. Fuel properties of hydroprocessed rapeseed oil. *Fuel* 2010;89:611–5.
- [31] Guzman A, Torres JE, Prada LP, Nunez L. Hydroprocessing of crude palm oil at pilot plant scale. *Catalysis Today* 2010;156:38–43.
- [32] Landauan MV, Herskowitz M, Givoni D, Laichter S, Yitzhaki D. Medium severity hydrotreating and hydrocracking of Israeli shale oil—testing of novel catalyst systems in a trickle bed reactor. *Fuel* 1998;77:3–13.
- [33] Huber GW, O'Connor P, Corma A. Processing biomass in conventional oil refineries: production of high quality diesel by hydrotreating vegetable oils in heavy vacuum oil mixtures. *Applied Catalysis A: General* 2007;329:120–9.
- [34] Kalnes T, Marker T, Shonnard D, Koers K. Green diesel and biodiesel a technoeconomic and life cycle comparison. In: *Proceedings of the 1st alternative fuels technology conference* February 18 2008 Prague, Czechoslovakia.
- [35] Aatola H, Larmi M, Sarjovaara T, Mikkonen S. Hydrotreated vegetable oil (HVO) as a renewable diesel fuel: Trade-off between NO_x, particulate emission, and fuel consumption of a heavy duty engine. SAE International copyright © 2008.
- [36] Neste Oil. NExBTL-second generation renewable diesel.
- [37] Collings J. Mind over matter the Sasol story: a half-century of technological innovation. Sasol: Johannesburg, South Africa; 2002.
- [38] Anton CVosloo. Fischer–Tropsch: a futuristic view. *Fuel Processing Technology* 2001;71:149–55.
- [39] Kamara Bukirwa Irene, Coetzee Johan. Overview of high-temperature Fischer–Tropsch Gasoline and diesel quality. *Energy & Fuels* 2009;23:2242–7.
- [40] Leckel D. Hydroprocessing Euro 4-type diesel from high-temperature Fischer–Tropsch vacuum gas oils. *Energy & Fuels* 2009;23:38–45.
- [41] Boerrigter H. 'Green' diesel production with Fischer–Tropsch synthesis. Slides for business-meeting Bioenergy, Platform Bio-energie. ECN, Petten. The Netherlands; 2002.
- [42] <<http://www.upm.com/en/Pages/default.aspx>>.
- [43] Norton P, Vertin K, Bailey B, Clark NN, Lyons DW, Goguen S, et al.. Emissions from trucks using Fischer–Tropsch diesel fuel. Reprinted from: alternative fuels; 1998.
- [44] Lamprecht D, Dancuart LP, Harrilall K. Performance synergies between low-temperature and high-temperature Fischer–Tropsch diesel blends. *Energy & Fuels* 2007;21:2846–52.
- [45] van Thuijl E, Roos CJ, Beurskens LWM. An overview of biofuel technologies, markets and policies in Europe; January 2003 ECN–C-03-008.
- [46] Yehliu K, Boehman AL, Armas O. Emissions from different alternative diesel fuels operating with single and split fuel injection. *Fuel* 2010;89:423–37.
- [47] Seyfried Frank, Volkswagen AG. Results of the RENEW project IP-502705. Project supported by European Commission under FP6. VOLKSWAGEN AG; September 2008.
- [48] European Committee for standardization. Automotive fuels–Diesel–Requirements and tests methods; January 2004.
- [49] <www.biofuels2g.gr>.
- [50] Xue J, Grift TE, Hansen AC. Effect of biodiesel on engine performances and emissions. *Renewable and Sustainable Energy Reviews* 2011;15:1098–116.
- [51] Bezergianni S, Chrysikou L. Oxidative stability of waste cooking oil and white diesel upon storage at room temperature. *Bioresource Technology* 2012;126:341–4.
- [52] Bezergianni S, Kalogianni A, Vasalos IA. Hydrocracking of vacuum gas oil–vegetable oil mixtures for biofuels production. *Bioresource Technology* 2009;100:3036–42.
- [53] Iki H, Iguchi Y, Koyama A. Applicability of hydrogenated palm oil for automotive fuels. In: *Proceedings of the 16th Saudi Arabia–Japan joint symposium*, Dhahran, Saudi Arabia; November 5–6 2006.
- [54] Sebos I, Matsoukas A, Apostolopoulos V, Papayannakos N. Catalytic hydroprocessing of cottonseed oil in petroleum diesel mixtures for production of renewable diesel. *Fuel* 2009;88:145–9.
- [55] Simacek P, Kubicka D. Hydrocracking of petroleum vacuum distillate containing rapeseed oil: evaluation of diesel fuel. *Fuel* 2010;89:1508–13.